CHEMISTRY LETTERS, pp. 2293-2294, 1987.

2,4,6-Tris(bis(trimethylsilyl)methyl)phenyl, a New Sterically Demanding Group for Kinetic Stabilization of Unstable Compounds

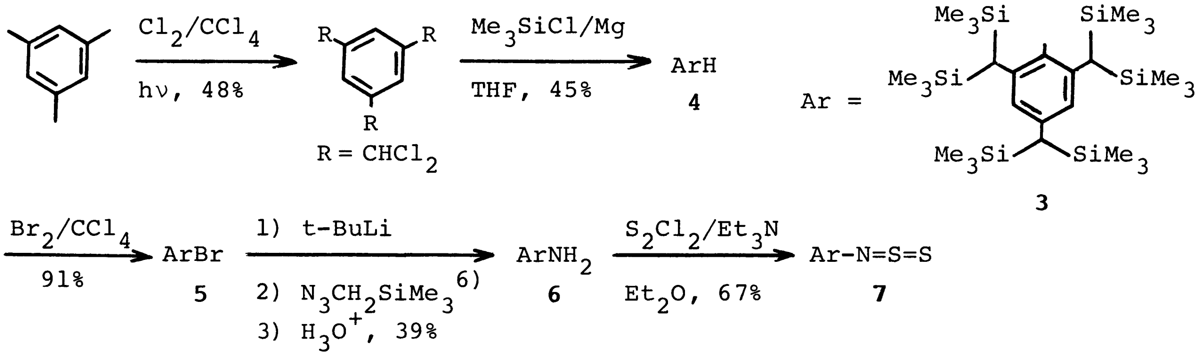
Renji OKAZAKI,* Masafumi UNNO, and Naoki INAMOTO
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Tokyo 113

The titled group (Ar) has been found to be very efficient for kinetic stabilization of a highly reactive N-thiosulfinyl group. The synthesis and the thermal and photochemical behavior of Ar-N=S=S are described.

In recent years many highly reactive, unstable chemical species such as compounds containing multiple bonds of heavier main-group elements have been isolated by taking advantage of kinetic stabilization due to sterically bulky groups. For example, 2,4,6-tri-t-butylphenyl (**1**) and tris(trimethylsilyl)methyl (**2**) groups have been successfully utilized for the synthesis of N-thiosulfinylanilines,1) diphosphenes,2) and thioaldehydes3) in these laboratories and others.4) There is a continuing need, however, for developing new sterically demanding groups of different types to study the relationship between the bulkiness of the groups and the reactivities of the compounds and to synthesize further novel types of compounds of high reactivity.

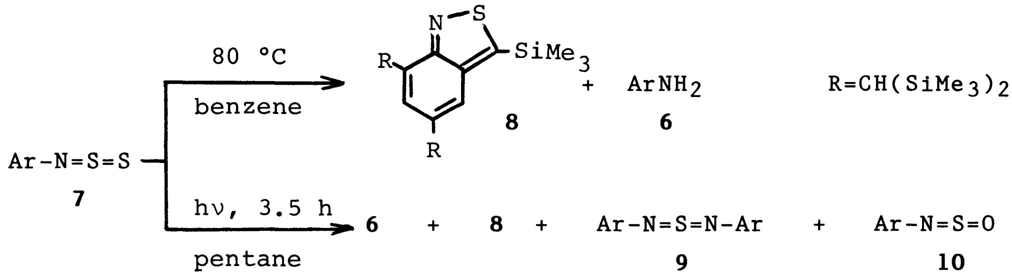
We report here that a new group, 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl (**3**) (denoted as Ar hereafter in this paper) is very useful as a steric protection group. The inspection of the molecular model suggests that the total bulkiness of the $CH(SiMe_3)_2$ group at the o-positions would retard the dimerization of ArX, where X is a highly reactive functional group, more efficiently than **1** although the position 1 in **3** is less crowded than that in **1** and hence the introduction and functionalization of the substituent at this position would be easy.

We chose the N-thiosulfinyl group as a highly reactive functional group to be



Scheme 1.

protected since we previously studied the synthesis and relative stability of some N-thiosulfinylanilines with different steric protection.[1b)] N-Thiosulfinylaniline **7** was successfully synthesized as shown in Scheme 1.[5)] **7** is thermally much more stable than previously reported 2,6-di-t-butyl-6-methyl- and 2,4,6-tri-t-butyl-N-thiosulfinylanilines; these N-thiosulfinylanilines were decomposed in refluxing benzene within 20 hours[1c)] while **7** was decomposed only after 1 week under identical conditions to give benzisothiazole **8** (71%)[5)] and aniline **6** (19%), suggesting that the Ar group functions as an efficient steric protection group.[7)]



The photolysis of **7** afforded sulfur diimide **9**[5)] (47%) and thiosulfinylaniline **10**[5)] (21%) as main products in addition to **6** (15%) and **8** (7%).[7)]

Further application of this new steric protection group **3** to the synthesis of compounds having other highly reactive functional groups is now actively under investigation.

References

1) a) Y. Inagaki, R. Okazaki, and N. Inamoto, Tetrahedron Lett., 1975, 4575; b) Y. Inagaki, R. Okazaki, and N. Inamoto, Bull. Chem. Soc. Jpn., 52, 1998 (1979); c) Y. Inagaki, R. Okazaki, and N. Inamoto, ibid., 52, 2002 (1979).

2) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 103, 4587 (1981).

3) R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, J. Chem. Soc., Chem. Commun., 1982, 1187; R. Okazaki, A. Ishii, and N. Inamoto, J. Am. Chem. Soc., 109, 279 (1987).

4) For example, see for **1**, A. H. Cowley, J. G. Lasch, N. C. Norman, and M. Pakulski, J. Am. Chem. Soc., 105, 5506 (1983); M. Hesse and U. Klingebiel, Angew. Chem., Int. Ed. Engl., 25, 649 (1986); J. Escudie, C. Couret, M. Andrianarison, and J. Satge, J. Am. Chem. Soc., 109, 386 (1987); for **2**, C. Eaborn, J. Organomet. Chem., 239, 93 (1982); A. H. Cowley, J. Escudie, Y. Madule, H. Ranaivonjatovo, J.-G. Wolf, Tetrahedron Lett., 24, 2769 (1983); M. Hesse and U. Klingebiel, Angew. Chem., Int. Ed. Engl., 24, 324 (1985).

5) New compounds **4**-**10** gave satisfactory analytical and spectral data, some of which were as follows (the NMR spectra were measured in $CDCl_3$ and expressed in δ). **4**: mp 244 °C(sublime); ^1H NMR 0.10(s, 54H), 1.29(s, 3H), 6.21(s, 3H); MS m/z 552(M^+), 464. **5**: mp 182.0-182.5 °C; ^1H NMR 0.03(s, 54H), 0.05(s, 18H), 1.31(s, 1H), 2.53(s, 2H), 6.41(s, 2H); MS m/z 630(M^+), 73. **6**: mp 147.0-148.3 °C; ^1H NMR 0.01, 0.02 (s each, 54H in total), 1.20(s, 1H), 1.38(s, 2H), 3.07(br, 2H), 6.27(s, 2H). **7**: deep purple crystals, mp 167.8-168.9 °C, ^1H NMR 0.02(s, 36H), 0.07(s, 18H), 1.26(s, 1H), 1.44(s, 2H), 6.46(s, 2H); ^{13}C NMR 0.84, 1.14, 25.68, 30.69, 133.21, 140.25, 143.61, 144.20; UV (hexane) 230(58600), 292sh(3870), 346(4860), 488(2490), 582(2320) nm; MS m/z 629(M^+), 73. **8**: ^1H NMR 0.02(s, 18H), 0.06(s, 18H), 0.50(s, 9H), 0.87(s, 1H), 1.53(s, 2H), 6.67, 7.04(ABq, J=1.8 Hz, 2H); MS m/z 523 (M^+), 73. **9**: ^1H NMR 0.02(s, 36H), 0.06(s, 18H), 1.35(s, 1H), 2.24(s, 2H), 6.45(s, 2H); FDMS m/z 1164(M^++2), 1162(M^+). **10**: ^1H NMR 0.03(s, 36H), 0.05(s, 18H), 1.38(s, 1H), 2.11(s, 2H), 0.42(s, 2H); MS m/z 613(M^+), 73.

6) K. Nishiyama and N. Tanaka, J. Chem. Soc., Chem. Commun., 1983, 1322.

7) The interesting mechanism for the thermolysis and photolysis of **7** will be discussed in a full paper.

(Received September 28, 1987)